

Hydrogen Diffusion in Amorphous Silicon Photovoltaic Solar Cells

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Signature

Any disclaimer(s) needed by the various DOE laboratories.

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Abstract

Hydrogen Diffusion in Amorphous Silicon Photovoltaic Solar Cells. RYAN QUILLER (Rensselaer Polytechnic Institute, Troy, NY 12180) H. BRANZ (National Renewable Energy Laboratory, Golden, CO 80401).

Hydrogenated amorphous silicon (a-Si:H) is used as a low-cost semiconductor in a range of consumer products because of low production costs. However, they have captured only 10% of the photovoltaic market because of their low efficiencies. This problem is caused in part by hydrogen diffusion, which occurs because a-Si:H is grown at elevated temperatures and because of light-induced degradation. Both problems cause the formation of dangling bond defects. Therefore, in order to better understand hydrogen diffusion in solar cells, a-Si:H i-p-i-n-i structures were made with deuterium tracer layers. These designs were annealed at temperatures similar to their deposition temperatures in order to analyze deuterium diffusion. Secondary ion mass spectrometry (SIMS) data was taken on each sample. A greater dynamic range of the SIMS data was attained than in similar previous experiments by Branz and Nelson since SiD₄ was used during deposition of the tracer layer instead of D₂. The SIMS concentrations and depths were scaled for consistency. Analysis focused on deuterium release rates. The results of this work support previous findings by Branz and Nelson that hydrogen moves as H⁺, H⁰, or H⁻ depending on the local Fermi level in the a-Si:H device. The activation energy for deuterium emitted from 120 Å from the p- and n-layers were 1.16 eV and 0.81 eV, respectively. These findings illuminate the nature of mobile hydrogen in a-Si:H and could lead to improved photovoltaic efficiencies.

Research Category: Materials Sciences

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Introduction

Solar cells are becoming more practical in utility-scale power plants as well as consumer products. They promise a clean source of limitless energy for the future. In the struggle to extend the use of a-Si:H solar cells, much attention has turned to increasing their efficiency. This form of solar cell is promising because of its superior optical absorption coefficient and abundant and safe raw materials (Maruyama, 1995). In addition, less energy is required to produce them than other photovoltaic devices such as crystalline silicon (c-Si).

One limitation on commercial applications of a-Si:H is defects, which are influenced by mobile hydrogen. The function of hydrogen in a-Si is to passivate threefold-coordinated silicon dangling bond defects and reduce the density of gap-state electronic defect levels (Branz et al., 1993). However, since a-Si:H is grown at temperatures around 200°C, H diffuses during growth and affects the device quality (Branz et al., 2001). Also, light-induced degradation is influenced by hydrogen diffusion and the formation of dangling bonds (Branz, 1999). Therefore, understanding the diffusion of hydrogen and where it becomes trapped is important in understanding its effect on a-Si:H growth, quality, and the creation of dangling bonds.

It was proposed in previous research that hydrogen diffuses as H^+ , H^0 , and H^- , depending on its location in the i-layer of a p-i-n structure, because of its internal electric field and local Fermi level. For charged mobile hydrogen, the electric field strongly influences the direction and distance of diffusion. Near the p-layer, E_f is near the valence band, and almost all of the hydrogen diffuses in the direction of the electric field as H^+ . Near the n-layer, E_f is near the conduction band, and almost all the hydrogen diffuses against the electric field as H^- . In the

center of the i-layer the local Fermi level gives H^0 and diffusion is equal in both directions (Nelson et al., 2001).

This research is aimed at using deuterium tracer layers at five locations in the i-layer to observe deuterium diffusion at varying anneal temperatures and times using SIMS. This will be done in order to understand H-diffusion during growth at similar temperatures and the mechanisms by which hydrogen moves. This will provide a greater understanding of how an electric field and the solubility in a-Si:H influences the amount and range of hydrogen diffusion at elevated temperatures. In previous work conducted at the National Renewable Energy Laboratory, D_2 was the gas used to create the tracer D-layer, but in this experiment, SiD_4 is used (Branz et al., 2001; Nelson et al., 2001). The advantage of using SiD_4 is that using D_2 produced deuterium concentrations of about 10^{20} cm^{-3} , while SiD_4 provides deuterium concentrations of about 10^{22} cm^{-3} . Since there is on the order of 100 times greater deuterium concentration, the signal-to-noise ratio is higher. This better dynamic range of signal provides an opportunity to gain a better understanding of the diffusing hydrogen.

The goal of this work is to learn more about hydrogen diffusion in a-Si:H in order to create more efficient a-Si:H photovoltaic solar cells.

Materials and Methods

To fabricate the a-Si:H structures, plasma-enhanced chemical vapor deposition (PECVD), a thin film deposition technique, was used. The advantage of PECVD is that it can alter layer compositions accurately, and it can be used on an industrial scale. This process was used to

create five different p-i-n structures, which were sandwiched by additional i-layers to avoid artifacts in SIMS data due to substrate and top surface interfaces. These devices were grown on c-Si substrates. Details of the thickness of each of the layers and the placement of the tracer D-layers in each of the five designs are shown in Figure 1. The total thickness of each design was about 3300 Å. During the PECVD, the SiH₄ flow rate was 45 sccm with a deposition pressure of 600 mTorr and a heater temperature of 220°C. The gas used for the i:D layer was SiD₄. Also, 5% PH₃ in H₂ and 3.1% B(CH₃)₃ in He were used in the deposition of the n- and p-layers, respectively. Each of the five designs was used to make seven samples using anneal temperatures of 190°C, 230°C, and 270°C and anneal times of 9.6 h, 48 h, and 240 h, although samples were not prepared for every possible time and temperature combination. Samples were not made at 190°C for 9.6 h because very little change would be expected take place. Likewise, samples were not made at 270°C for 240 h because so much of the deuterium would diffuse that the deuterium tracer-layer might be depleted.

SIMS profiling data was taken on H, D, and O negative secondary ions from one crater and a (Cs₂D)⁺ complex as positive secondary ions from another crater for each sample. A 14.5keV Cs⁺ beam was used as the primary ion source for sputtering the H, D, and O. Likewise, a 5.5 keV Cs⁺ beam was used as the primary ion source for sputtering the (Cs₂D)⁺. A mechanical profilometer was used to measure the depth of the resulting crater and set the depth scale for each SIMS profile.

To account for inaccuracies in the mechanical profilometer's measurements, the depth scale for each SIMS profile needed to be shifted and rescaled appropriately. Examples of raw SIMS data

for oxygen and deuterium are shown in Figure 2. Oxygen peaks were present due to impurities in the deposition gases, and did not move during annealing because of the strong Si-O bonds. Therefore, the oxygen peaks from each of the samples within a design could be shifted and scaled to match each other. This was done using a program to minimize the sum of the squares of the distances between the three peaks in each plot. Since deuterium data was taken from the same crater as that for oxygen, the deuterium data was shifted and scaled with the corresponding oxygen data to create a relative depth scale as shown in Figure 3. The $(\text{Cs}_2\text{D})^+$ plots were then scaled to match the depth values of corresponding features on the adjusted deuterium plots. Since SIMS had a better depth resolution for the $(\text{Cs}_2\text{D})^+$ complex than for D, the $(\text{Cs}_2\text{D})^+$ profile was used to analyze deuterium diffusion in the samples. These curves were integrated up to the c-Si interface spike in the data and scaled in the y-direction to maintain constant integral values in order to account for noise because deuterium is conserved.

Using the scaled $(\text{Cs}_2\text{D})^+$ SIMS profiles, it was possible to find the amount of deuterium that diffuses into either the p-layer (N_D^P) or the n-layer (N_D^N) for a given temperature. This is done by integrating the concentration in the layer of interest and subtracting the corresponding integral of the sample before annealing. These values were then plotted against the anneal time. These plots were fitted to a function of the form $N(t) = N_0(1 - \exp(-t/\tau))$, where N_0 is a constant representing the saturation value of the layer in question, and t is the anneal time. The first step in this process was to find N_0 . By rearranging the equation mentioned above, it is clear that $\ln(1 - N/N_0) = -t/\tau$ should be linear in t . Therefore, by plotting $\ln(1 - N/N_0)$ versus N and varying N_0 , the value of N_0 can be established when the plot becomes linear. Once N_0 was found, fitting to $N(t)$ allowed the time constant, τ , to be determined. An example is shown in Figure 6 for design

L756. Then, $\ln(\tau)$ plotted against $1/T$ was fit to a function of the form, $\tau(T) = \tau_0 \exp(E_a/(kT))$, where k is Boltzmann's constant, T is the anneal temperature, and τ_0 is constant. This type of plot is shown in Figure 7 for the same design. This determines the activation energy, E_a , required to detrapp hydrogen.

Results

Several of the scaled SIMS profiles of $(Cs_2D)^+$ are shown in Figures 3 and 4. After minimizing the squares of the distances between the peaks in the oxygen profiles and scaling the corresponding deuterium data, it was found that during the depth scaling of $(Cs_2D)^+$ to the D data, the corrections in the x-values were usually about 10%. It was also determined that the corrections in the $(Cs_2D)^+$ concentrations were usually about 20%. This was found when the data was y-scaled in order to match integral values for each sample with the same design.

Figures 4 and 5 contain grouped plots in order to emphasize particular aspects of the depth profiling. These figures are plots of concentration versus depth. Figure 4 shows the effect of diffusion with anneal time for each of the five designs at 230°C. Likewise, Figure 5 shows the effect of the anneal temperature on diffusion for each design at the fixed anneal temperature of 240 hrs. The plots are aligned in such a way that the distance between each of the as grown peaks is separated by the distances shown in Figure 1. The corresponding $(Cs_2D)^+$ data in each design are aligned to be consistent with its as grown peak. Note that the amplitude of the plots decrease with anneal time and temperature while the widths tend to increase. These plots illustrate the deuterium movement based on its original location in the p-i-n structure. Also, the plots indicate how deuterium moves relative to the internal electric field, which points from the

n-layer on the right side of the plots to the p-layer on the left side. Deuterium movement toward the p-layer is noticeable for designs L759 and L760, while movement toward the n-layer is evident in L756 and L757.

The activation energies to detrap deuterium at a distance of 120 Å from each of the doped layers was calculated. For the L756 design, which is close to the the n-layer, the activation energy is 0.81 eV. For the L760 design, which is close to the p-layer, the activation energy is 1.16 eV.

Discussion and Conclusions

Trends in the data from Figures 4 and 5 indicate that deuterium preferentially diffuses in the direction of the electric field in all samples for designs L759 and L760, which suggests the mobile deuterium is in the form of D^+ . On the other hand, these figures also show that deuterium preferentially diffuses against the electric field in all samples for the designs L756 and L757, which suggests the mobile deuterium is in the form of D^- . The samples for L758 did not show any preferential direction of diffusion, which supports the idea that D^0 is the mobile form of deuterium.

These results support the conclusions of previous work (Branz et al., 2001; Nelson et al., 2001). However, due to the better resolution of these results, this experiment related more information concerning how the mobile state of hydrogen is affected by solubility and the internal electric field. There is still some doubt concerning the whether or not mobile hydrogen near the doped layers is charged because of solubility effects.

In addition, since the activation energy to detrapp hydrogen near the p-layer is higher than it is near the n-layer, it should be easier for hydrogen to accumulate in the n-layer. This was supported by the fact that the concentrations in the n-layer were usually higher than the concentrations in the p-layer when comparing samples with D-tracer layers at the same distance from the doped layers, such as L756 and L760, which are 120 Å from the n- and p-layer, respectively.

Increased understanding of hydrogen movement is helpful in understanding a-Si:H growth and the creation of dangling bond defects during illumination. These results can be used to observe trends important to hydrogen loss during growth, which may be related to defect formation during illumination. The anneal time and temperature effects illustrated in this research may allow better understanding of dangling bond formation, thus allowing better quality a-Si:H photovoltaic devices to be made, which in turn allows greater solar cell efficiency.

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References

- Branz, H.M., Asher, S.E., & Nelson, B.P (1993, March 15). "Light-Enhanced Deep Deuterium Emission and the Diffusion Mechanism in Amorphous Silicon." The American Physical Society, 47(12), 7061-7065.
- Branz, H.M. (1999, February 15). "Hydrogen Collision Model: Quantitative Description of Metastability in Amorphous Silicon." Physical Review B, 59(8), 5498-5512.
- Branz, H.M., Reedy, R., Crandall, R.S., Mahan, H., Xu, Y., & Nelson, B.P (2001, August). "Fermi-Level Dependence of the Charge State of Diffusing Hydrogen in Amorphous Silicon." Journal of Non-Crystalline Solids.
- Maruyama, E., Tsuda S., & Nakano, S. (1995). "Industrialization of Amorphous Silicon Solar Cells and Their Future Applications." Solid State Phenomena, 44-46, 863-880.
- Nelson, B.P., Xu, Y., Reedy, R.C., Crandall, R.S., Mahan, H.A., & Branz, H.M. (2001). "Determination of the Mobile-Hydrogen Charge State in Hydrogenated Amorphous Silicon." Mat. Res. Soc. Symp. Proc., 664, A28.2.1-A28.2.6.

Figures

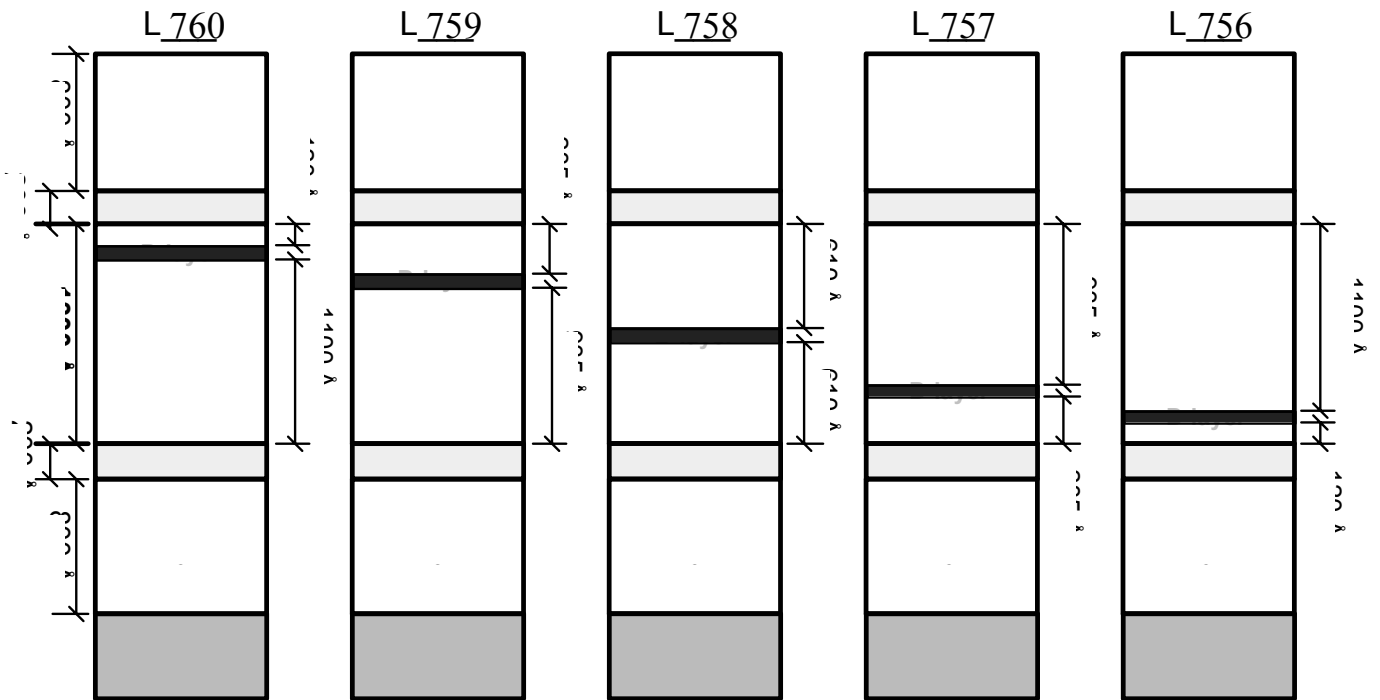


Figure 1. Growth designs for each of the samples. In each sample, the D-layer was made with SiD_4 and is 80 Å thick.

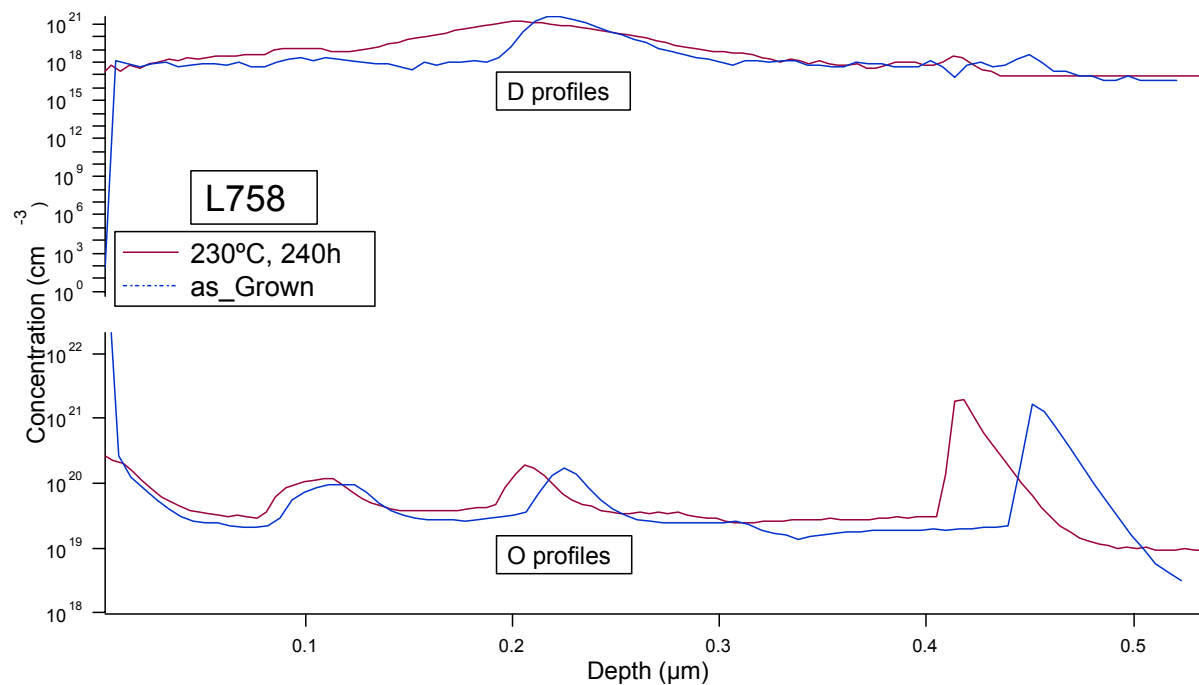


Figure 2. Examples of unscaled SIMS oxygen profiles (bottom) and deuterium profiles (top). The sample represented by the red profiles was annealed at 230°C for 240 hrs, and the sample represented by the blue profiles was not annealed. Both samples come from design L758.

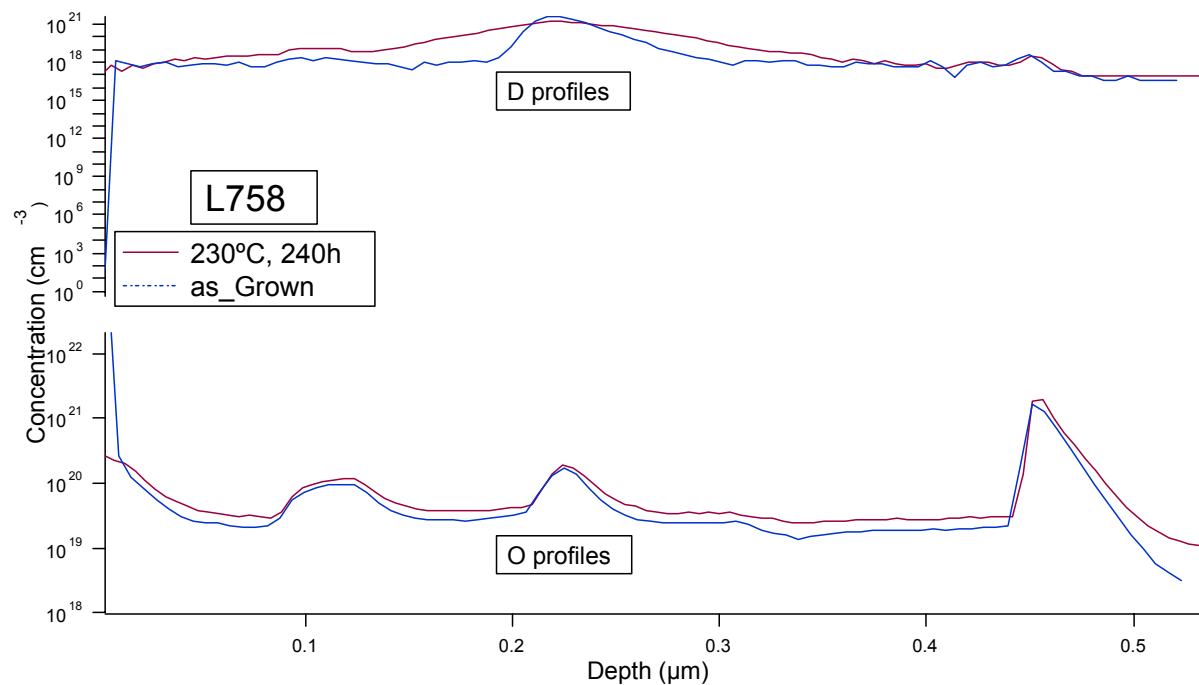


Figure 3. Scaled SIMS oxygen profiles (bottom) and deuterium profiles (top). The sample represented by the red profiles was annealed at 230°C for 240 hrs, and the sample represented by the blue profiles was not annealed. Both samples come from design L758.

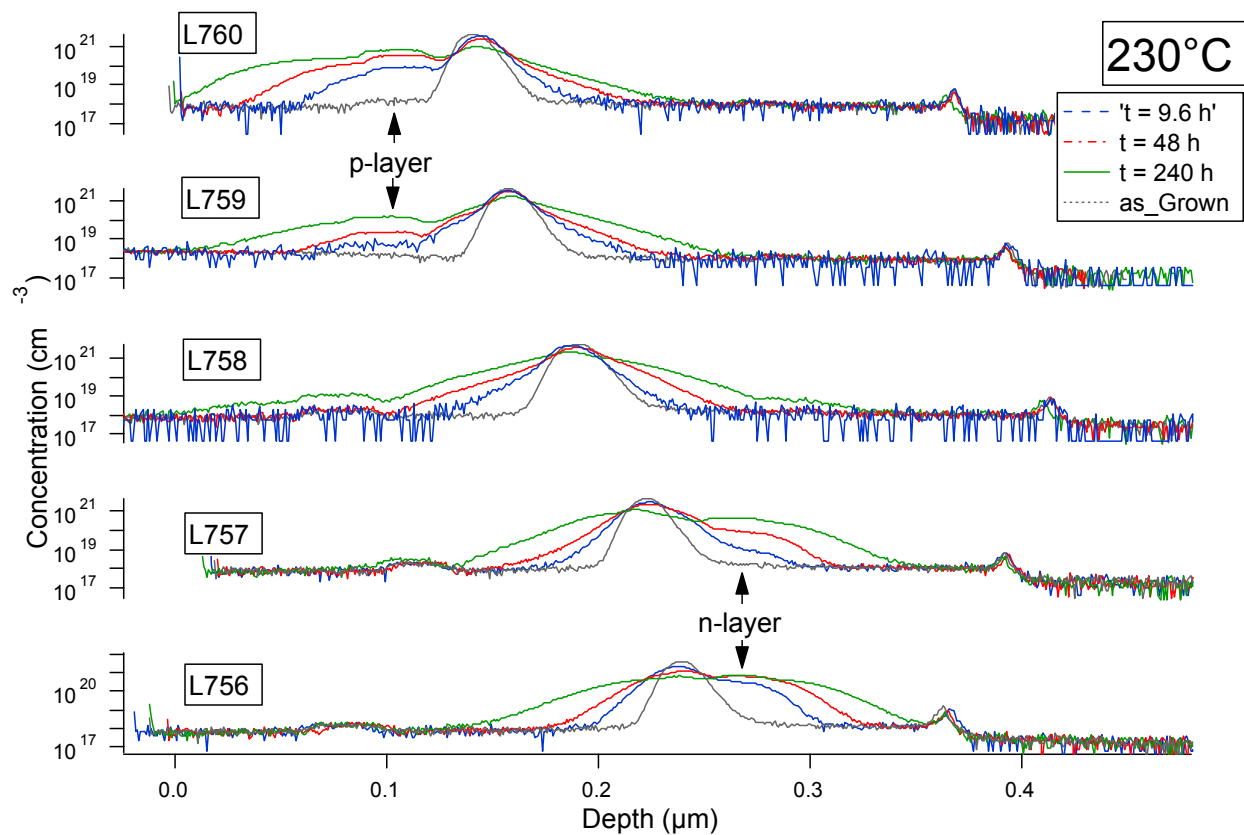


Figure 4. $(\text{Cs}_2\text{D})^+$ concentrations vs. depth for anneals at 230°C . Anneal times were 0 hrs (gray), 9.6 hrs (blue), 48 hrs (red), and 240 hrs (green). L760 are profiles for samples with the D-tracer layer closest to the p-layer, while L756 are profiles for the samples with the D-tracer layer closest to the n-layer. The internal electric field points from right to left.

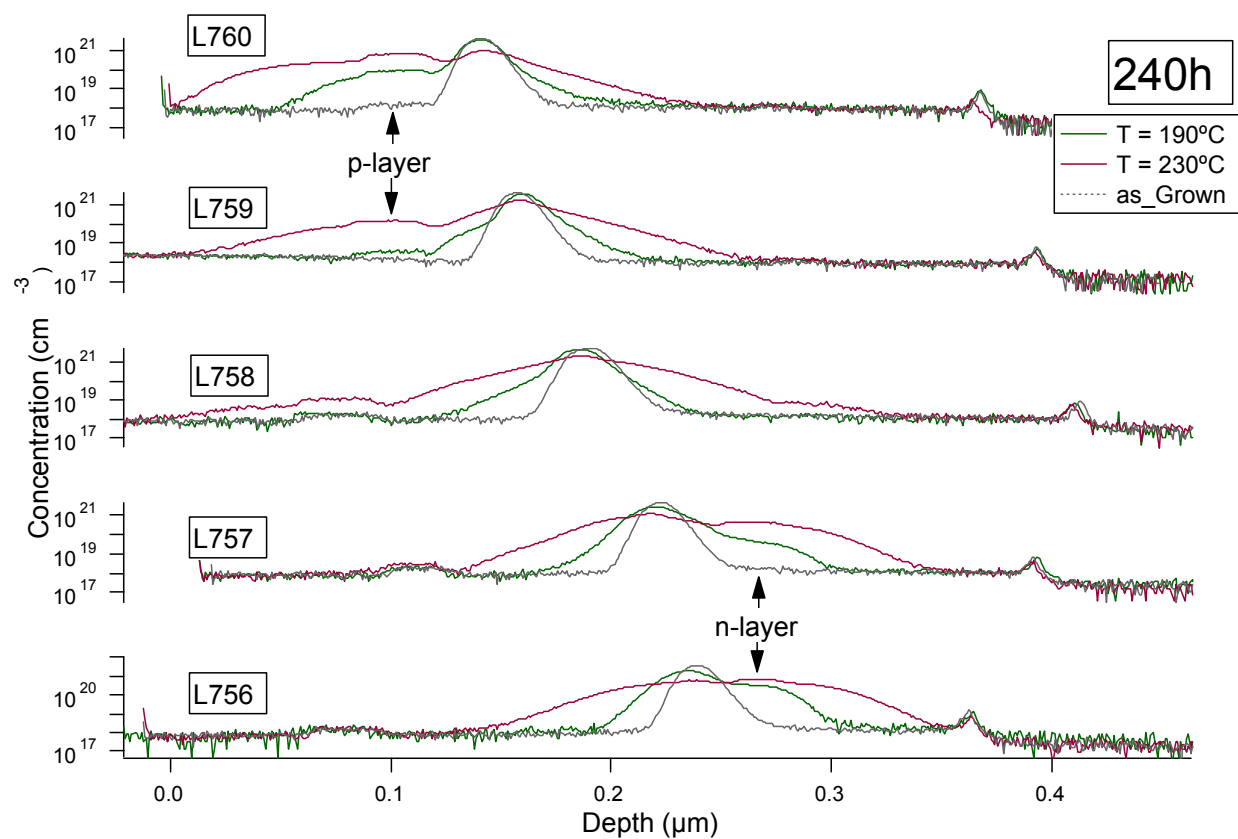


Figure 5. $(\text{Cs}_2\text{D})^+$ concentrations vs. depth for 240 hr anneals. Anneal temperatures were 190°C (red) and 230°C (green). The gray profiles were samples before annealing. L760 are profiles for samples with the D-tracer layer closest to the p-layer, while L756 are profiles for the samples with the D-tracer layer closest to the n-layer. The internal electric field points from right to left.

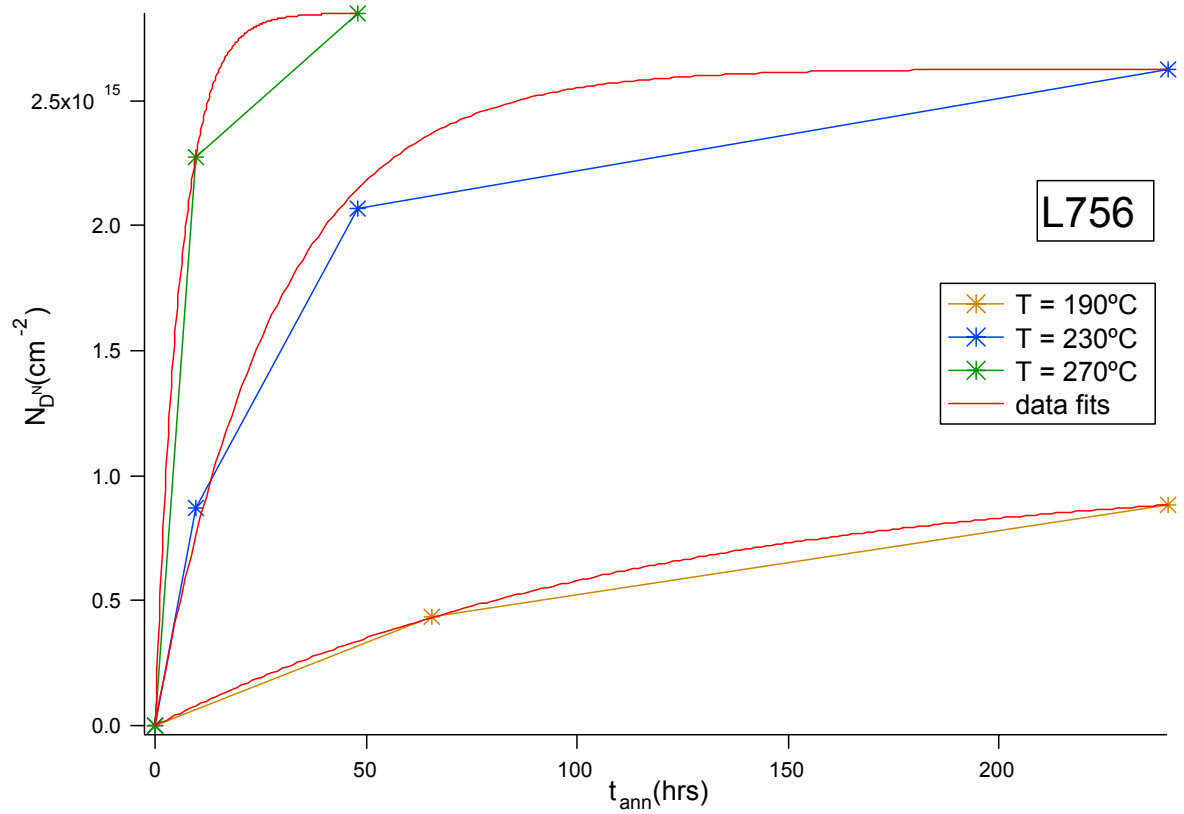


Figure 6. Concentration of deuterium in the n-layer vs. anneal time. The yellow, blue, and green lines represent anneal temperatures of 190°C, 230°C, and 270°C, respectively. Each set of data came from design L756. The red lines are the fits to each set of data.

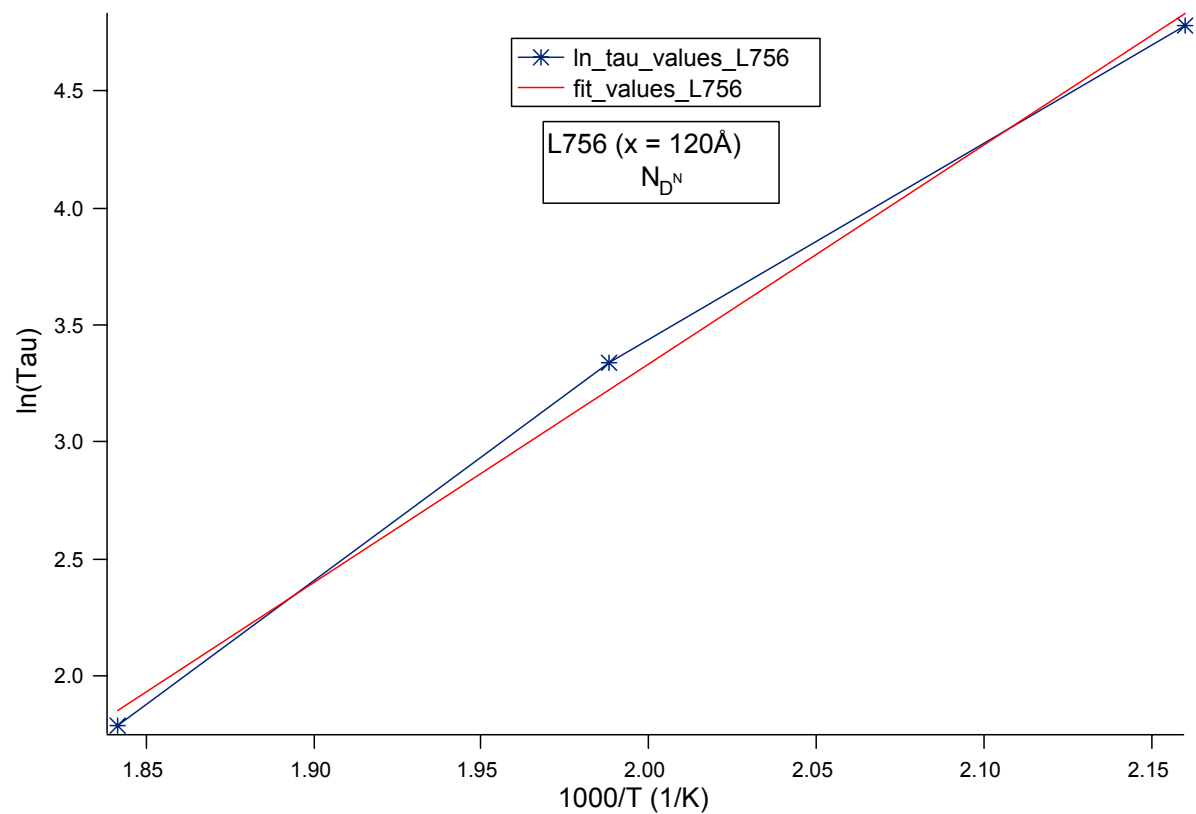


Figure 7. The natural logarithm of the time constants found for the increase in deuterium in the n-layer for design L756 vs. 1000 divided by the anneal temperature. The blue and red lines represent the value obtained from the original data and the fit to those values, respectively.